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Temperature dependence of thermal pressure

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Abstract : Three models are developed to study the temperature dependence of thermal pressure. These models are based on the (i) approximation that the product of the coefficient of the volume thermal expansion α and isothermal bulk modulus K_T remains constant, (ii) Suzuki formulation of thermal expansivity, (iii) Kumar formulation of equation of state. The results obtained for five materials are compared with the experimental data. It is found that the results based on the (αK_T) constant are smaller than the experimental data. On the other hand, the results based on the Suzuki formulation are higher. The results based on the Kumar formulation are found to lie in between these two sets of the data and are in good agreement with the experimental data. The similar trend of variation found for all the materials, demonstrates the superiority of the model based on the Kumar formulation.

Keywords Thermal pressure, thermal expansivity, equation of state

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1. Introduction

Equation of state (EOS) plays an important role in understanding the properties of matter under extreme conditions of pressure and temperature. Under static condition, the EOS of a solid reads as follows [1]

$$P = -\frac{dE}{dV}, \tag{1}$$

where P is the pressure, E the lattice potential energy and V the volume. From eq. (1), it is evident that the lattice potential energy is entirely volume dependent. The determination of potential energy is very important for the study of equation of state and related properties. Most of the theoretical attempts made for this purpose, may be divided in two categories : (i) those which involve the use of the theory of interionic potentials, either two-body or three-body [2], (ii) those which are entirely free from the use of potential model [3]. It has been observed that methods based on the theory of interionic potentials are very tedious [2] and involve a lot of computational work in addition to various approximations. On the other hand, the second one is free from these difficulties [2]. Due to simplicity, we have adopted second method in the present paper. To include the effect of temperature in eq. (1), two approaches have also been used in the literature [4]. In first approach, the temperature effect is incorporated by adding the thermal pressure term in the eq. (1). In second approach, one can use directly eq. (1) at high temperature by modifying parameters [4]. Thus, the second approach needs the values of input parameters at higher temperatures which may not be available for a particular material. On the other hand, the first approach is free from such difficulties and needs the input parameters at initial temperature. In this sense, the first approach seems to be simple as compared with the second. Using this approach, the determination of thermal pressure needs the vibrational parts of thermodynamic functions of a solid at a given temperature and pressure. The actual normal vibrations in crystals are very complicated in nature and it is even more difficult to evaluate the variation of vibrational frequencies with change in volume. In order to circumvent these difficulties, approximate models such as due to Einstein and Debye were developed which have been critically reviewed by Tosi [1]. For

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the purpose of EOS, two approximations have been found to be very useful [1].

The assumption that the vibrational energy of a solid be a purely temperature dependent function, leads to the so-called Hildebrand approximation [1]. Within the framework of this approximation, the expression for thermal pressure P_{Th} may be obtained using calculus as follows :

$$\frac{\partial P}{\partial T} \quad \frac{\partial P_{Th}}{\partial T} = \alpha K_T \tag{2}$$

Upon integration we get,

$$P_{Th} = \alpha K_T (T - T_0). \tag{3}$$

Eq. (3) gives the value of P_{Th} under the approximation that (αK_T) is independent of temperature T.

Using the quasi-harmonic approximation, the expression of thermal pressure reads as follows [1]

$$P_{Th} = \frac{1}{V}\sum \gamma_j E_{Th}, \tag{4}$$

where E_{Th} is the energy arising from temperature excitation, called the thermal energy. If we take γ_j out of the sum by assuming that γ_j are equal to each other and to γ. This gives

$$P_{Th} = \frac{\gamma}{V} E_{Th} \tag{5}$$

Eq. (5) is known as Mie-Gruneisen expression for thermal pressure and γ is called Gruneisen parameter. Thus, Mie-Gruneisen EOS is written as

$$PV = -VE_0'(v) + \gamma E_{Th}, \tag{6}$$

where $E_0'(v) = dE/dV$. Both these approximations have been found to be good for ionic solids at the temperatures comparable to, and somewhat higher than the Debye temperature. Mie-Gruneisen theory has been used by Suzuki [5] to study the thermal expansivity of solids. The theory of high pressure high temperature EOS has also been formulated by Kumar [6-8]. Due to the simplicity and soundness of the theory, it is being frequently used in the literature [9, 10]. Thus, it becomes legitimate and may be useful to present a comprehensive analysis of these relations to predict the temperature dependence of thermal pressure. Critical comments on the relations and their equivalence is also presented. The method of analysis is presented in Section 2. The results obtained for a number of materials are discussed in Section 3.

2. Method of analysis

Suzuki [5] expanded the quantity PV of eq. (6) and obtained what became known as Suzuki equation [11]. The detailed analysis is available elsewhere [5] and the mathematical form reads as follows [5, 11].

$$\frac{V}{} - \frac{\left[1 + 2k - (1 - 4kE_{Th}/Q)^{1/2}\right]}{2k} \tag{7}$$

where $k = (K_{T0}' - 1)/2$ and $Q = K_{T0} V_0/\gamma_0 . K_{T0}$ and K_{T0}' are the isothermal bulk modulus and its first order pressure derivative respectively, V the volume and subscript o refers to their value at $P = 0$ and $T = 300$ K. Using eq. (5), we can rewrite eq. (7) as follows :

$$\frac{V}{V_0} - 1 = \frac{1 - \left[1 - \left\{2(K_{T0}' - 1)/K_{T0}\right\} P_{Th}\right]^{1/2}}{(K_{T0}' - 1)}. \tag{8}$$

Eq. (8) gives

$$P_{Th} = K_{T0}\left(\frac{V}{V_0} - 1\right) - \frac{1}{2} K_{T0}(K_{T0}' - 1)\left(\frac{V}{V_0} - 1\right)^2. \tag{9}$$

Eq. (9) seems to be very simple and may be used to study the temperature dependence of thermal pressure, provided that the corresponding values of V/V_0 are known.

The theory of high-pressure-high temperature has also been reported by Kumar [6-8]. It was found that the theory predicts the properties of solids from atmospheric pressure upto the structural transition pressure by varying the temperatures from room temperature upto the melting temperature. A comparative study demonstrated that the theory is far better than the other relations available in the literature and agrees with the experimental data quite well [6-8]. The detailed analysis is available elsewhere [7, 8] and mathematical form reads as follows [7, 8]:

$$\frac{V}{V_0} = 1 - \frac{1}{A}\ln\left[1 + \frac{A}{K_{T0}}(P - P_{Th})\right], \tag{10}$$

where $A = (K_{T0}' + 1)$. At $P = 0$, eq. (10) reads as follows:

$$\frac{V}{V_0} = 1 - \frac{1}{A}\ln\left(1 - \frac{A P_{Th}}{K_{T0}}\right). \tag{11}$$

By neglecting the higher order terms, it can be shown that

$$-\ln(1 - x) = 1 - (1 - 2x)^{1/2}. \tag{12}$$

Thus, eq. (11) may be rewritten in a similar form to that of Suzuki relation (eq. 8)

$$\frac{V}{V_0} - 1 = \frac{1 - \left[1 - \left\{2(K_{T0}' + 1)/K_{T0}\right\} P_{Th}\right]^{1/2}}{(K_{T0}' + 1)} \tag{13}$$

or

$$P_{Th} = K_{T0}\left(\frac{V}{V_0}-1\right)-\frac{1}{2}K_{T0}\left(K'_{T0}+1\right)\left(\frac{V}{V_0}-1\right)^2. \quad (14)$$

Now, if we compare eqs. (9) and (14), it is very clear that the term $(K'_{T0}-1)$ appearing in the Suzuki formulation (eq. 9), has been replaced by $(K'_{T0}+1)$ in the Kumar formulation (eq. 14). This difference arises due to the two different methods used in their derivations.

3. Results and discussion

Thus, we have three different formulae (eqs. 3, 9 and 14) for the determination of temperature-dependence of thermal pressure in solids. In these equations, there are three model parameters viz., α_0, K_{T0} and K'_{T0}. Actually, these are defined as room temperature and zero pressure (atmospheric pressure) values. Thus, these are equilibrium values and therefore taken as fixed during the entire calculation. Eq. (3) is very simple and it gives directly the values of P_{Th} at a required temperature. In eq. (3), it has been assumed that the product (αK_T) is independent of temperature. The results thus obtained, are reported in Figures 1-5. The application of eq. (9) and (14) needs the values of V/V_0 at corresponding temperatures. For the determination of V/V_0 as a function of temperature, the theoretical as well as experimental methods are readily available. Anderson and Isaak [12] have compiled such data for a number of solids in the form

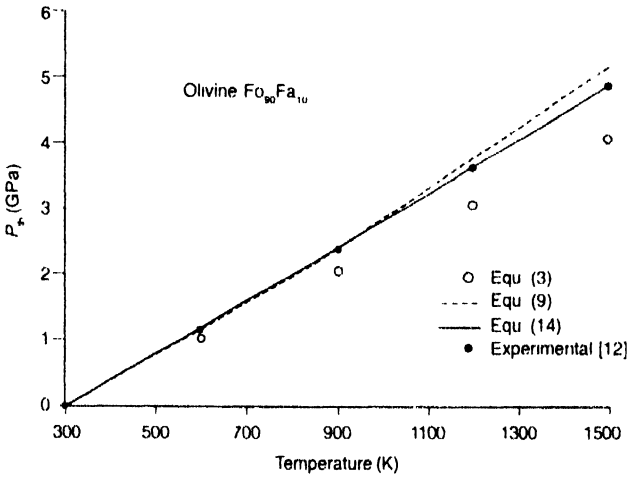

Figure 3. Variation of thermal pressure with temperature

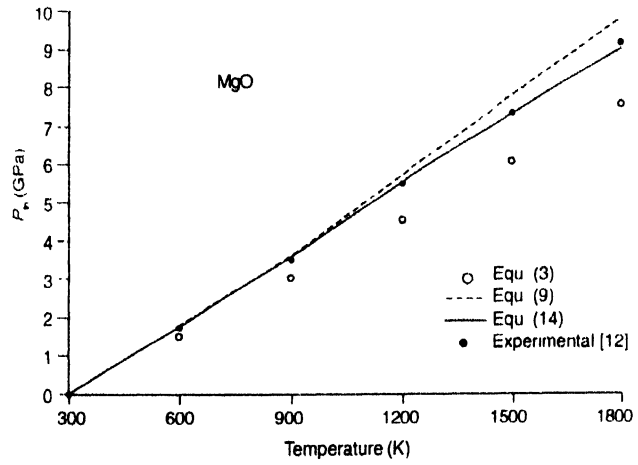

Figure 1. Variation of thermal pressure with temperature

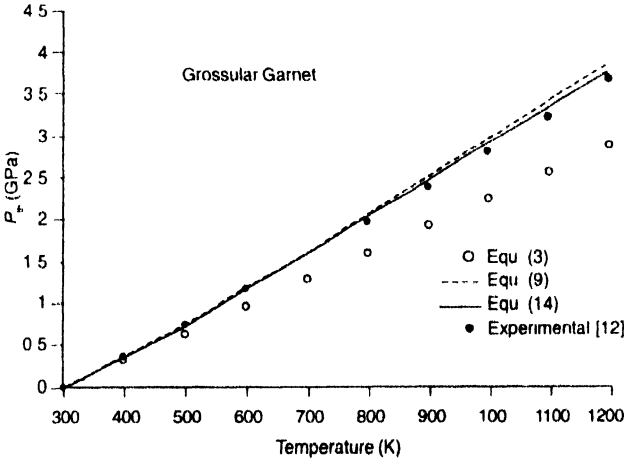

Figure 4. Variation of thermal pressure with temperature

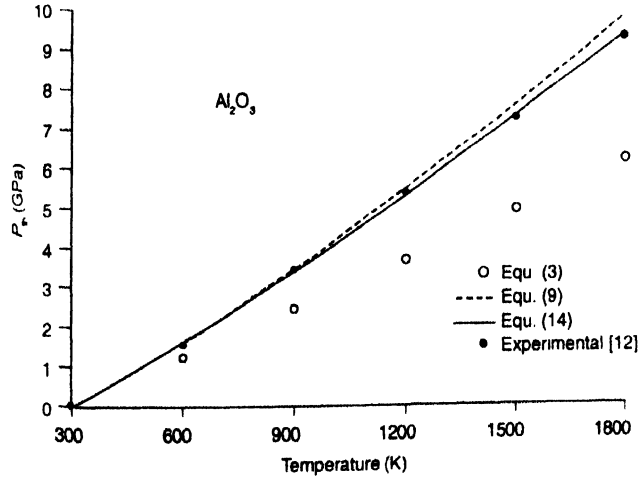

Figure 2. Variation of thermal pressure with temperature.

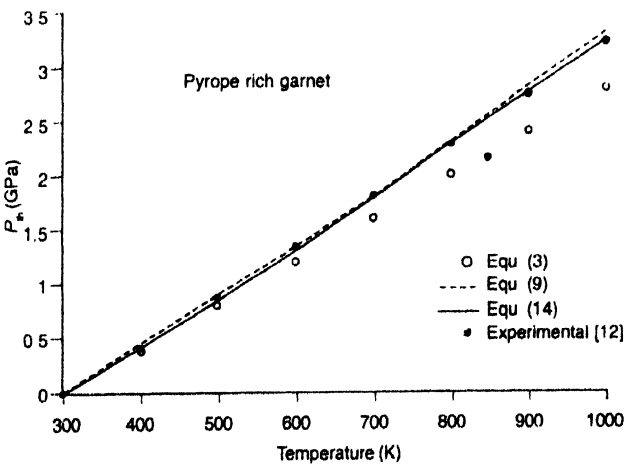

Figure 5. Variation of thermal pressure with temperature

of density. We used these data for the present calculations. These calculations also need the values of K'_{T0} which have been compiled from literature [13, 14], as given in Table 1 along with other input data [12]. The range of K'_{T0} shown in Table 1, arises from individual experimentalists who have chosen a value of K_{T0} and accepted the corresponding value of K'_{T0} to fit their P, V data. In such cases, an average value of K'_{T0} is used for present calculations.

Table 1. Values of input parameters, α_0 (in 10^{-5} K^{-1}), K_{T0} (in GPa) and K'_{T0}.

	α_0 [12]	K_{T0} [12]	K'_{T0} [13, 14]
MgO	3.12	161 6	3 87 - 4.84
Al_2O_3	1.62	252 0	4.28 - 4.38
Olivine Fo_{90} Fa_{10}	2.66	128.0	4 6
Grossular garnet	1.92	166.6	4 25
Pyrope rich garnet	2 36	169 4	4.74 - 5.43

The results thus obtained are reported in Figures 1-5 along with the experimental data [12]. It is found that the results obtained by eq. (3) are smaller as compared with the experimental data [12]. On the other hand, the results obtained using eq. (9) are higher. The results obtained from eq. (14) have been found to lie in between the data obtained from eqs. (3) and (9). These are in good agreement with the experimental data [12]. To confirm the situation, we have considered five materials. The similar trend of variation found in all the cases confirm the superiority of eq. (14) as compared with eqs. (3) and (9). The maximum deviations are found at highest temperatures; we have therefore, calculated the percentage deviations at highest temperatures for all the materials considered in the present work and reported in Table 2. These percentage deviations confirm the above conclusion.

It should be discussed that eq. (3) is based on the approximation that (αK_T) is independent of T. It seems that due to this reason, the results obtained by eq. (3) deviate from the experimental data [12]. Eq. (9) comes from Suzuki relation which is based on Mie-Gruneisen theory. It has been discussed in the literature [15] that Mie-Gruneisen equation is good for some solids but not for all. For this, we quote the following statements from Anderson and Isaak. "Thus, we believe that Mie-Gruneisen EOS may be an insecure base for derivations" [15, p 66] and "Mie-Gruneisen EOS is a very poor approximation" [15, p 83] It should also be mentioned that Suzuki model is based on the Taylor expansion of potential energy term in eq. (6). During this expansion, only the second order term has been considered by neglecting higher order terms. This approximation must introduce an error at high temperatures as discussed by Wang and Reeber [16]. Probably, due to these reasons, the results obtained by eq. (9) deviate from the experimental data [12].

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Table 2. Percentage deviations in thermal pressure at highest temperatures using eq. (3), Suzuki formulation (eq 9) and Kumar formulation (eq 14)

MgO T = 1800 K			Al_2O_3 T = 1800 K			Olivine Fo_{90} Fa_{10} T = 1500 K			Grossular garnet T = 1200 K			Pyrope rich garnet T = 1000 K		
Eq. (3)	Eq (9)	Eq. (14)	Eq (3)	Eq (9)	Eq (14)	Eq. (3)	Eq (9)	Eq. (14)	Eq (3)	Eq (9)	Eq (14)	Eq. (3)	Eq (9)	Eq (14)
17.8	6.8	1.4	33.8	5.6	0 86	16 4	5 6	0 40	21.9	4 88	2 17	13.3	2 5	0 30

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